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1 January 2001

OPTICS  
COMMUNICATIONS

Optics Communications 187 (2001) 235–247

www.elsevier.com/locate/optcom

# Laser-induced surface and bulk reorientation of the director in azo-dye-doped liquid crystal cells

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Received 27 April 2000; received in revised form 14 August 2000; accepted 7 November 2000

## Abstract

The director reorientation in the liquid crystals (LCs) cells initiated by the *trans–cis* isomerization of azo-dyes was studied with the aid of pump–probe–beam experiments. Two different types of the samples were used, namely, a planar aligned LC layer, doped with an azo-dye, placed between substrates coated with rubbed poly(vinyl alcohol) (PVA) films, and an undoped LC layer placed between substrates, one of which (input) was coated with an untreated azo-polymer film and other one was coated with rubbed PVA film. The cells were excited with nanosecond pulses of the second harmonic of an Nd:YAG laser. By comparing the reorientation dynamics with the help of dynamic holography method in both samples it was established that the values of development times of the orientational effects were the same. The reorientation develops within 15–17  $\mu$ s and the efficiency of the orientational gratings is 13–15%. In both kinds of samples the director orientation on the output surface with the rubbed PVA coating was not changed after irradiation. Contrary, the orientation of the director on the input substrate was changed in both cases. In case of a LC cell with azo-modified surface the reorientation is due to the photoisomerization of the azo-polymer film. In case of the cell with azo-dye-doped LC layer the photoisomerization of dye in the bulk of LC together with PVA film rearrangement on input substrate exert an influence on the director reorientation. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 78.20.Jq; 42.70.Df; 78.20.C; 83.70.Jr

Keywords: Liquid crystal; Azo-dye; Reorientation; Photoisomerization; Nonlinear optics

## 1. Introduction

Azo-dye-containing media have been actively studied and developed during the last few years

because of the potential ability to use them in various optical applications, i.e. nonlinear optics, phase conjugation, information recording and storage, optical switching, etc. Objects under the investigation include azo-polymers [1–6] and nematic liquid crystals (LCs) [7–11] doped with azo-dyes whose molecules undergo photochemical transformation (*trans–cis* isomerization) at light

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illumination. The configurational changes of dopant dye molecules lead to changes of optical properties of a polymer or LC medium. Such materials can serve as media for recording dynamic and static holograms with a resolution not worse than  $100 \text{ lines mm}^{-1}$  under the action of radiation of low power (a few milliwatts) cw lasers [2,12]. The efficiency of information recording in LC cells with azo-modified polymeric surface or in cells filled with azo-dye-doped LCs depends on set of factors, in particular, the chemical structure of azo-dyes, surface anchoring energy, the parameters of laser radiation (its polarization and intensity) and the exposure time. The devices based on this effect have high sensitivity but they have slow response time (a few minutes). A fastening of an optical response of the LC devices is an actual task from practical point of view.

The mechanism of photoinduced reorientation in the polymer films had been studied in some detail [13,14]. It consists of two stages, the first of them is anisotropic depletion of the angular distribution of *trans*-isomers as a result of *cis*-isomer accumulation along the light polarization direction (angular hole burning). After this, the molecules rotate during the *trans*–*cis*–*trans* isomerization cycle (angular redistribution) that results in orthogonal orientation of the molecular azo-fragment ( $-\text{N}=\text{N}-$ ), with respect to the electrical light field [15]. After the consequent *cis*–*trans* retransition, the *trans*-isomers orient in the direction different in comparison with initial one. In azo-dye-doped LCs, the initial angular distribution of the highly dichroic dye *trans*-isomers is defined by the orientation of the matrix. In the course of photoexcitation a rotation of the LC-director in the bulk, induced by photoisomerization of the azo-dye molecules, can proceed along a three-dimensional trajectory [11]; in addition, the reorientation sign depends on the beam propagation direction [9]. Different reorientation signs have been explained by the fact that the resulting optical torque produced by *trans*- and *cis*-isomers can be either positive or negative [10].

In many cases studied, the reorientation in the bulk of azo-dye-doped LC and the reorientation induced with azo-modified surface were created under stationary conditions of *trans*–*cis*–*trans*

photoisomerization at excitation of cw lasers. The mechanism of *trans*–*cis* isomerization can be induced under the action of the short pulses from a powerful laser because the characteristic time of the conformational transformations of the azo-molecules is equal to several picoseconds [16]. Earlier we had shown the possibility of isothermal phase transition (disordering of the LC layer as a result of the *cis*-isomers accumulation in it) induced by second harmonic radiation from ruby laser in liquid-crystalline azo-compounds [17].

In this paper, the LC-director reorientation had been studied under saturation conditions of the *trans*–*cis* transitions of azo-containing fragments of a rigid polymeric film and also of azo-dyes dissolved in a more mobile LC medium. Intensive photoexcitation was achieved with nanosecond laser pulses of the second harmonic (SH) of a Nd:YAG laser. Dynamic holography and polarimetric technique were used to study the reorientation kinetics with the same conditions of excitation in two kinds of samples, the first of them was a planar azo-dye-doped LC layer oriented with the mechanically rubbed poly(vinyl alcohol) (PVA) films on both substrates, and the second one was an undoped LC layer placed between substrates coated with an untreated azo-dye-doped copolymer DR1-PMMA (one substrate) and a rubbed PVA film (other substrate). In this work we demonstrate that the *trans*–*cis* isomerization of the azobenzene dye molecules in the bulk of the dye-doped LC sample together with a re-arrangement of PVA coating play an important role in the director reorientation. At high power irradiation, a PVA film on the input substrate (to the incoming pump beam) can change its orienting properties and, *ea ipso*, exert an influence on the director rotation. Then we are able to compare the orientational response of the LC cell with azo-dye-doped LC layer and the LC cell with an azo-modified surface on the input substrate. In both samples the LC molecules have a strong homogeneous planar alignment close to the PVA output surface, which remains unchanged after illumination. But the orientation of the director on the input substrate is changed in both cases after irradiation. In the cells with azo-dye-doped LC layer an easy-orientation axis can arise along the input

surface as a result of its modification. In the LC cell with an azo-polymer film there is initial easy-orientation axis, which changes its position during exposure. The anchoring energy on input surface before SH illumination and the change of it during the course of irradiation was estimated in both cases. The comparison of the dynamics of the orientational effects in the two kinds of samples shows the same development times of the reorientation.

## 2. Experiment

### 2.1. Liquid crystal samples

Two types of samples were prepared: the cells **I** and the cells **II**.

The first of them were the cells with azo-dye-doped LC layer which had planar orientation created by mechanically rubbed PVA films. The cells were filled with a nematic 4-pentyl-4'-cyano-biphenyl (5CB) and were doped with the addition of the dye 4-dimethylamino-4'-nitroazobenzene (DMANAB). The structure formula and the absorption spectrum of DMANAB in 5CB are shown in Fig. 1. DMANAB is characterized by a

high degree of ordering in the nematics [18], its order parameter  $S$  in the planar 5CB layer is equal to 0.59. The LC-dye compositions were prepared with the dye concentrations 0.19 wt.% (absorption coefficient components  $\alpha_{\parallel} = 268 \text{ cm}^{-1}$ ,  $\alpha_{\perp} = 50 \text{ cm}^{-1}$ ), 0.35 and 0.5 wt.%. These cells' thickness  $L$  was equal to 50  $\mu\text{m}$ .

The second samples were LC cells in which one of the substrates (input) was coated with an untreated azo-polymer film and the output one with a mechanically rubbed PVA film. The copolymer poly(disperse red 1 methacrylate-co-methyl methacrylate) (DRI-PMMA) (Fig. 1) was used. The coatings were prepared by pulling the substrate from a solution of copolymer in dichloromethylene (3 wt.%). To the polymer backbone the fragment of dye 4-diethylamino-4'-nitroazobenzene (disperse red DR1) (24 wt.%) was chemically joined. The dyes DMANAB and DR1 are from the same series of the azo-dyes. The absorption spectrum of the azo-polymer in the visible region is analogous to that of DMANAB in 5CB, the only difference is a shift of 10 nm to short wave region. The azo-polymer film thickness was approximately 0.4  $\mu\text{m}$ . Intrinsic absorption of the azo-polymeric film exhibits a small absorption dichroism,  $d = 0.15$ , which is caused by the film preparation

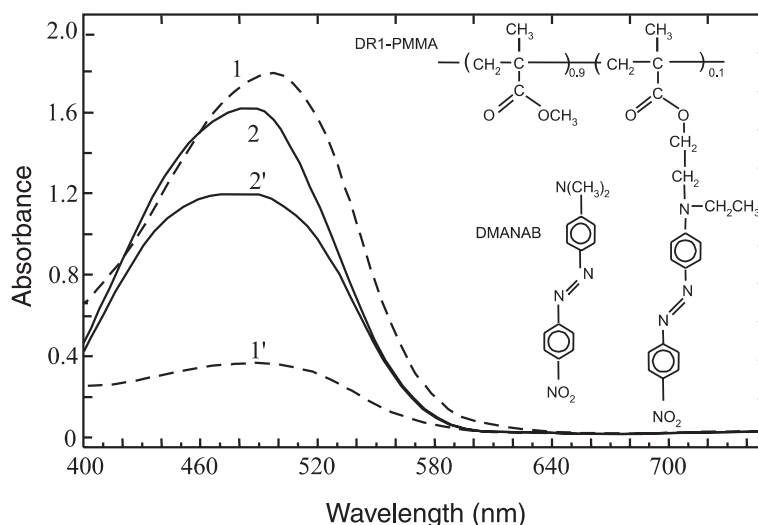


Fig. 1. Chemical structures of azo-dye DMANAB and azo-polymer DRI-PMMA and absorption spectra of (1,1') DMANAB in 5CB and (2,2') azo-polymer film. The spectra 1–1' and 2–2' correspond to the geometries  $\mathbf{E} \parallel \mathbf{L}$  and  $\mathbf{E} \perp \mathbf{L}$ , respectively. For the azo-polymer film the direction  $\perp$  corresponds to the direction of pulling.

method. The cells were filled with undoped 5CB. The LC cell thickness was 10  $\mu\text{m}$ . Stable orientation of the cells was established itself for about 2 h. There emerged a twisted structure with an angle of twisting  $\phi'$ . It was equal to  $18^\circ$  when the direction of pulling of the azo-polymer film and the rubbing direction  $\mathbf{n}$  of the PVA film on output substrate were orthogonal.

## 2.2. Photoinduced reorientation in azo-dye-doped liquid crystal

Fig. 2 illustrates the experimental setup for the investigation of the photoexcitation and relaxation kinetics of the LC reorientation by using crossed polarizers with a single pump beam excitation (screen on) and by the dynamic grating method (screen off). The Q-switch Nd:YAG laser operating in the SH regime (monopulse energy  $E = 1$  mJ, pulse energy with amplifier 5.5 mJ, pulse duration  $\tau = 10$  ns,  $\lambda = 533$  nm) was used as a pump source. Dynamics of the light transmission of the LC cells after illumination was monitored by the change of intensity of the He–Ne probe laser ( $P = 1$  mW,  $\lambda = 633$  nm). Probe beam passed through the LC cell located between crossed polarizers  $\mathbf{P}_1$  and  $\mathbf{P}_2$  in the center of the excited zone and its intensity was detected by a photomultiplier that was placed behind an analyzer.

The reorientation dynamics of the cells **I** was studied at the excitation with a single pump beam. The exciting beam was linearly polarized with a vector  $\mathbf{E}_{\text{Nd}}$ . There was an angle  $\theta$  between the

polarization vector  $\mathbf{E}_{\text{Nd}}$  and the layer director  $\mathbf{L}$  in the azimuthal plane (in substrates plane). The layer director  $\mathbf{L}$  was parallel to the polarizer optical axis  $\mathbf{P}_1$  and to polarization vector of the probe beam  $\mathbf{E}_{\text{He-Ne}}$ . Using such geometry of the interaction we detected the director rotation in the bulk of the cells **I** in azimuth plane. At the angle  $\theta = 45^\circ$ , the greatest rise in the transmission of a probe beam was observed. Fig. 3a shows the transmittance dynamics of the LC cell with the azo-dye concentration of 0.19%. After the exposure, the photodetector registers a buildup of the probe beam intensity with characteristic time  $\tau_1 \approx 1$  ms, followed by the relaxation during  $\tau_2 \approx 200$  ms (Fig. 3a). These time constants were obtained by fit of the experimental relaxation curve with biexponential model  $A = -A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , which includes two exponents with opposite signs. Assuming that the probe beam diameter (1 mm) is much larger than the cell thickness ( $L = 50$   $\mu\text{m}$ ), the decay time of orientational mode in the LC layer could be estimated using the relationship  $\tau_\theta = \gamma L^2 / \pi^2 K_{22}$  [19], where  $\gamma$  is the rotational viscosity and  $K_{22}$  is the elastic constant for a twist deformation of the director. For 5CB, the constant  $K_{22}$  is equal to  $4.0 \times 10^{-12}$  N [20] and the value of  $\gamma$  is about  $0.0096$  N s m $^{-2}$  [21]. Then the relaxation time of  $\tau_\theta \approx 600$  ms is obtained, which agrees well with the experimental value.

In the cells **I** having more high DMANAB-dye concentration (0.5 wt.%) a static recording of a region with nonplanar orientation was observed after an exposure with a single beam of Nd:YAG

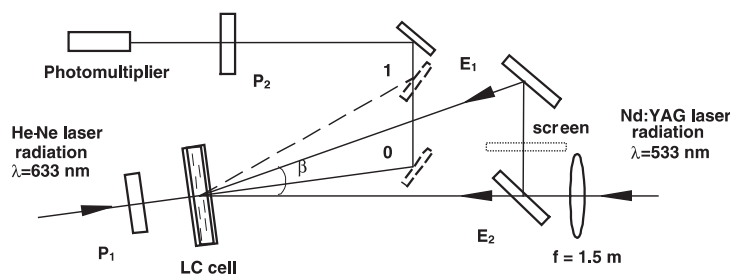


Fig. 2. Experimental arrangement for the investigation of optical response of the LC cells with single pump beam (screen on) and by diffraction gratings methods (screen off). The pump beam from Nd:YAG laser operating in the SH regime was used for the excitation of the LC cell. The probe beam from He–Ne laser was used for the investigations of both the transmittance of a cell placed between polarizers  $\mathbf{P}_1$  and  $\mathbf{P}_2$  (screen on) and the intensity of the first diffraction order (screen off).

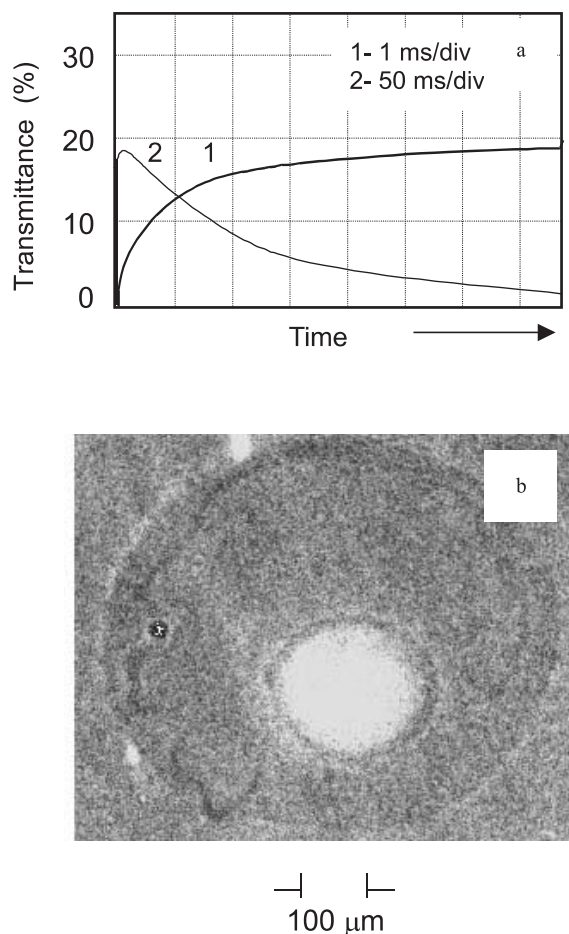


Fig. 3. (a) The probe-beam transmittance vs time for the cell **I** placed between crossed polarizers on different time scales. Excitation energy density is  $40 \text{ mJ cm}^{-2}$ . (b) The static reorientation in the LC cell with azo-dye concentration of 0.5% induced by single pulse. Excitation energy density is  $80 \text{ mJ cm}^{-2}$ .

laser, equipped with amplifier ( $P = 80 \text{ mJ cm}^{-2}$ ). This can be seen in the photograph in Fig. 3b. Examination with a polarization microscope has revealed that the LC cell in this interaction region possessed a twist orientation with a twist angle of  $12^\circ$ . Such orientation is created as a result of photoinduced changes in the PVA orienting agent applied onto the input substrate. The output surface does not change after exposure. This fact can be explained by the losses of monopulse energy in molecular layers nearest to input substrate because of the high absorption coefficient of the cell ( $705 \text{ cm}^{-1}$ ).

The details of the photoinduced reorientation in the bulk of the cells **I** have been studied by the dynamic grating method. The beam of an Nd:YAG laser was split into two beams of equal intensity interfered in the cell (Fig. 2). The beams were focused with a long focal length lens to a spot 2 mm in diameter. The angle of convergence  $\beta$  of the waves  $E_1$  and  $E_2$  was sufficiently small and varied from  $1^\circ$  to  $3^\circ$ . The grating vector was parallel to the LC layer director **L**. The polarizations of the pump waves  $E_1$  and  $E_2$  were rotated by an angle of  $13^\circ$  from the layer director in azimuthal plane. Fig. 4 reports the oscillograms of the probe beam intensity variation of the first diffraction order on different time scales. The typical time trace is shown in Fig. 4a. The response of the LC cell occurs in several stages. We studied the relaxation of the photoinduced process to distinguish its characteristic times. In accordance with multi-exponential model the change of diffracted signal intensity can be described by the sum of several exponents:  $A = A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) + A_4 \exp(-t/\tau_4)$ . Fig. 4a demonstrates that in the course of the monopulse excitation, the amplitude of the diffracted beam sharply increases in 10 ns, then, after some relaxation it rises up again during  $\tau_2 \approx 15 \mu\text{s}$ . The decay consists of one fast and two slow components, with relaxation times of  $\tau_1 = 6 \mu\text{s}$  (trace c),  $\tau_3 = 4 \text{ ms}$  (b) and  $\tau_4 = 30 \text{ ms}$  (b), respectively. At high-power laser excitation, the change of the refractive indexes of azo-dye-doped LC cell can occur due to the both thermal [22–24] and

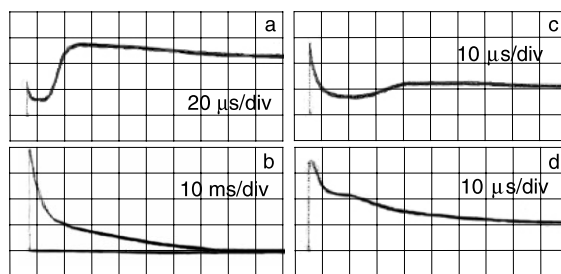


Fig. 4. The grating decay in the cell with nematic 5CB doped with DMANAB (cell **I**) after nanosecond laser pulse excitation on different time scales. Excitation energy density is (a,b)  $60 \text{ mJ cm}^{-2}$ , (c)  $15 \text{ mJ cm}^{-2}$  and (d)  $30 \text{ mJ cm}^{-2}$ .

conformational nonlinearity [17,25], which bring about a lowering of the order parameter. There are different orientational effects [26–31], which also contribute to the change of the diffracted beam intensity. The decay times of the thermal and orientational modes and the isomer diffusion time constant can be estimated using the following expressions [23]:  $\tau_T = \Lambda^2/4\pi^2 D_T$ ,  $\tau_\theta = \gamma \Lambda^2/4\pi^2 K$  and  $\tau_{CF} = \Lambda^2/4\pi^2 D_{CF}$  [25].  $D_T$  and  $D_{CF}$  are the coefficients of thermal diffusion and diffusion of the isomers dissolved in LC, respectively. For 5CB,  $D_T \approx 1.8 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  [24] and a value of  $D_{CF}$  for LC is  $\sim 1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  [25]. Then, for a grating period of  $\Lambda = 10 \text{ }\mu\text{m}$  (at which the diffraction efficiency of the orientational grating is maximum (Fig. 4b)), we obtain values close to the experimental ones:  $\tau_1 \sim \tau_T = 14 \text{ }\mu\text{s}$ ,  $\tau_3 \sim \tau_\theta = 6 \text{ ms}$  and  $\tau_4 \sim \tau_{CF} = 160 \text{ ms}$ . We assume that heating of the LC layer and the *cis*-isomers accumulation in them take place during the monopulse, i.e. the development times of both thermal nonlinearity and conformational one are defined by the pulse duration. In the Fig. 4a, one can see the thermal decay at the beginning of the trace, followed by the build-up and the decay of the reorientation. Here, the amplitude of the diffracted signal on the grating, which describes the orientational effect, is higher than the amplitude of thermal component. The traces in Fig. 4b demonstrate the decay of both processes the reorientation and the diffusion of the isomers. The response of LC to the powerful laser irradiation depends on the intensity of the exiting beam. The oscillograms (c), (d) and (a) present the competition of the thermal and the reorientation effects at an increasing of excitation energy.

The comparison of the orientational gratings efficiency in the different experimental geometries was carried out via a polarimetric method (Fig. 5). When the polarization vectors of the pump waves  $\mathbf{E}_1$  and  $\mathbf{E}_2$  have some small angle (within  $13^\circ$ ) with the layer director  $\mathbf{L}$ , and the probe beam polarization  $\mathbf{E}_3$  is perpendicular to  $\mathbf{L}$ , the grating efficiency is much higher than that to be found for other interaction geometries, namely  $\mathbf{E}_1$  and  $\mathbf{E}_2$  perpendicular to  $\mathbf{L}$ . This grating efficiency value was found to be  $\eta = 13\%$  (Fig. 5a, curve 1). Considerable diffraction scattering ( $\eta \approx 8\%$ ) occurs in

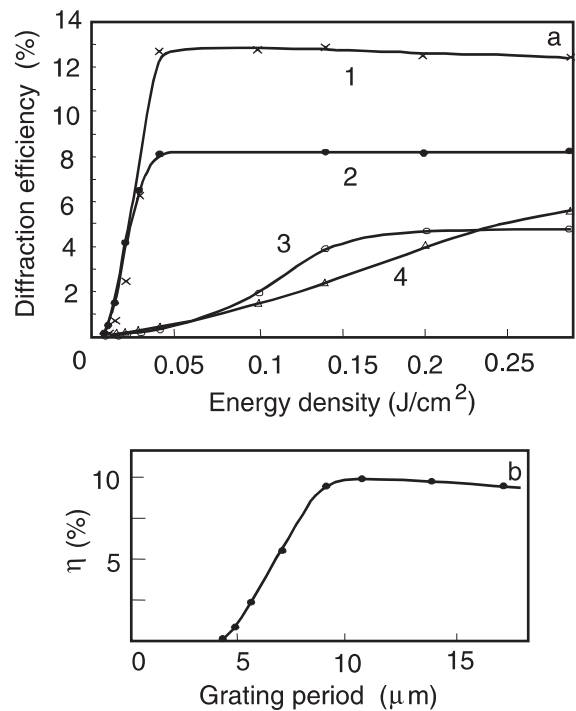


Fig. 5. Probe beam diffraction efficiency  $\eta$  of orientational grating recorded in LC doped with DMANAB as function of both (a) a pump energy density and (b) a grating period. The experimental geometries are: (1) The angle between the pump beams polarizations  $\mathbf{E}_1$  and  $\mathbf{E}_2$  and layer director  $\mathbf{L}$  is  $13^\circ$ ,  $\mathbf{E}_3 \perp \mathbf{L}$ ; (2) The angle between the pump beams polarizations  $\mathbf{E}_1$  and  $\mathbf{E}_2$  and layer director  $\mathbf{L}$  is  $13^\circ$ ,  $\mathbf{E}_3 \parallel \mathbf{L}$ ; (3)  $\mathbf{E}_{1,2} \perp \mathbf{L}$ ,  $\mathbf{E}_3 \parallel \mathbf{L}$ ; (4)  $\mathbf{E}_{1,2} \perp \mathbf{L}$ ,  $\mathbf{E}_3 \perp \mathbf{L}$ .

the  $\mathbf{E}_3 \parallel \mathbf{L}$  geometry. The diffracted beam intensity can have a contribution from the interference of o- and e-waves passing through the twist deformation, which arises due to the existence of an angle between the probe beam polarization direction and the director direction at the input surface. This can explain the higher grating amplitude recorded in the  $\mathbf{E}_3 \perp \mathbf{L}$  geometry. At radiation energy densities  $30\text{--}300 \text{ mJ cm}^{-2}$  (Fig. 5, curves 1 and 2), the dependences of orientational gratings efficiency on excitation energy demonstrate saturation.

### 2.3. Alignment in the LC cells with azo-containing polymeric surface

Under the same experimental conditions investigations were carried out to determine the re-



sponse times of the director reorientation initiated by the photoisomerization of an azo-modified polymeric surface in the cells **II**. In the initial state the LC sample has a twist deformation of the director with a twist angle  $\phi'$ . Experiments showed that linearly polarized Nd:YAG laser radiation generates a region with a twist orientation which is different from the initial one. These changes have been studied by examination of the transmission of the probe beam through a cell placed between polarizers in such a manner that the rubbing direction  $\mathbf{n}$  on the entrance surface to the probe beam (input surface for a pump beam) coincides with the polarizer axis  $\mathbf{P}_1$  whilst the analyzer axis  $\mathbf{P}_2$  is rotated by an angle  $(90^\circ + \phi')$  resulting in minimal transmission of the cell (Fig. 2). At such geometry, in accordance with the Mauguin mode, the polarization vector of the He–Ne laser follows the rotation of the director and we can find the value of twisting angle by a rotation of the analyzer. If the Nd:YAG laser radiation polarization vector  $\mathbf{E}_{\text{Nd}}$  is parallel to  $\mathbf{n}$ , we observe further twisting of the director relative to its initial position ( $\phi > \phi'$ ). For  $\mathbf{E}_{\text{Nd}} \perp \mathbf{n}$ , an opposite situation occurs, i.e. the twist angle decreases ( $\phi < \phi'$ ), in other words, the LC molecules tend to be “repelled” from the polarization vector. This angle is dependant on the excitation power and it can achieve a full twist or planar reorientation, i.e. we can observe a layer director untwist to  $\phi = 0^\circ$  or twist-up to  $\phi = 90^\circ$ . Fig. 6 shows the dependence of the twist angle  $\phi = \phi' + \Delta\phi$  on the pump beam energy density, which was obtained 5 s after irradiation of a cell at an initial twist angle of  $\phi' = 18^\circ$ . There exists a threshold value  $P_t = 30 \text{ mJ cm}^{-2}$  from which the reorientation starts its own active development. Fig. 7 demonstrates the development of the photoinduced reorientation effect when the cell was exposed to a train of pulses with a pulse energy density of  $80 \text{ mJ cm}^{-2}$  and 1 Hz frequency. The eighth pulse forms a static record of the spot (Fig. 7c) which stored itself for several months. What is peculiar to this spot is the formation of differently oriented structures in the center and along the edges. If the initial orientation of the director is twisted by  $18^\circ$ , then, after exposure to the beam with the polarization vector directed along the rubbing direction  $\mathbf{n}$ , the central

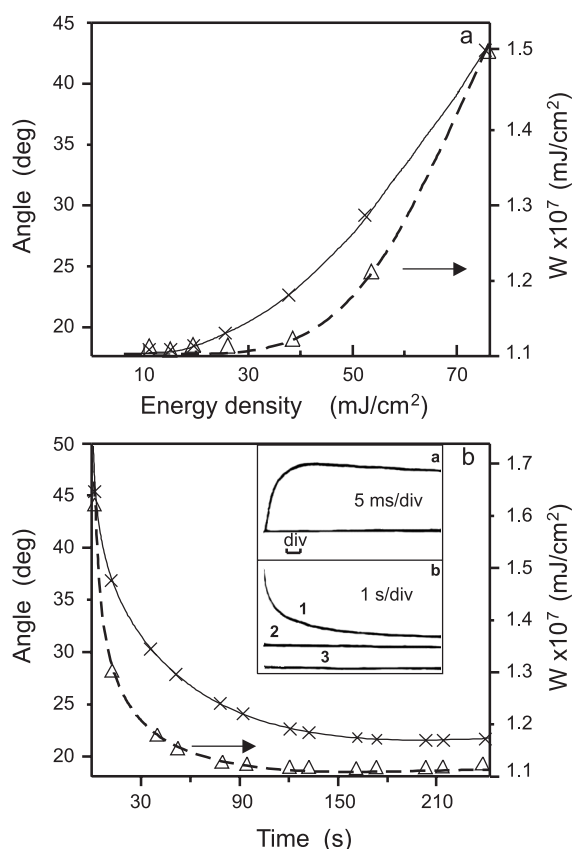


Fig. 6. The twist angle  $\phi$  of the director in the LC cell with azo-modified surface (—) and the anchoring energy density  $W$  (---) as functions of (a) pump energy density (5 s after irradiation) and (b) time (pump energy density is  $80 \text{ mJ cm}^{-2}$ ). Insert shows the oscillograms of the cell transmittance change after exposure. The trace 1 is obtained after a termination of monopulse, the trace 2 is obtained after 30 s. The trace 3 is recorded before the excitation.

part of the spot is twisted up by a further  $63^\circ$  while its outer part is untwisted to  $0^\circ$ .

The dynamics of the reorientation was studied by a single pulse excitation at energy density  $P = 60 \text{ mJ cm}^{-2}$ . As it is evident from the oscillogram in Fig. 6b (insert), the reorientation buildup time constant calculated in accordance with biexponential model is about 2 ms and agrees well with the time of the director rotation development in the bulk of azo-dye-doped LC (Fig. 3a, curve 1). Further decay proceeds in two stages: the cell transmission decreases rapidly during  $\sim 900 \text{ ms}$

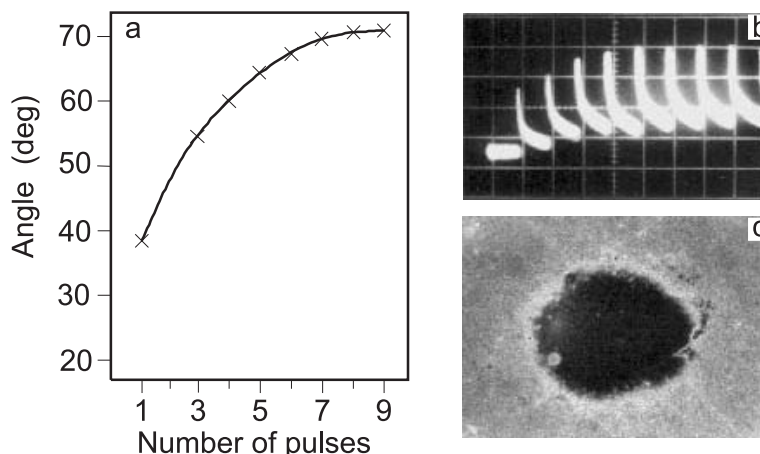


Fig. 7. The accumulation of photoinduced reorientation effect in LC cell with azo-modified surface at excitation with pulses train at pulse energy  $80 \text{ mJ cm}^{-2}$  and frequency 1 Hz. (a) The dependence of the twist angle  $\phi$  vs number of pulses. (b) The oscillogram of pulses train which induces photoreorientation. (c) A static recording formed by eighth pulse.

and then slowly recovers its initial value in several minutes.

Both dynamic and static orientational gratings were recorded in the cells **II** by the interference field of the Nd:YAG laser radiation. The polarization vectors  $\mathbf{E}_1$  and  $\mathbf{E}_2$  of the pump beams and the grating vector were placed in the same plane that the direction of a rubbing of output substrate  $\mathbf{n}$ . The probe beam polarization  $\mathbf{E}_3$  was orthogonal to the last direction. Fig. 8a reports the change of orientational grating efficiency at an excitation energy increasing and temporal changes in the LC cell response. The grating period  $\Lambda$  was  $10 \mu\text{m}$ . The diffraction efficiency of the grating was found to be 15%, which is comparable with that found in the cells **I**. From the oscillograms in Fig. 8b–e one can notice the several photoinduced relaxation processes with characteristic times of  $5 \mu\text{s}$  (trace a), 1 ms (d) and 0.5 s (e). In comparison with relaxation curves for the cells **I** the first time constant represents the time of thermal diffusion. In the case of the cells **II** heating of the azo-polymeric film and the LC layer located near its surface can occur. After thermal relaxation, the grating efficiency does not fall but instead rises during  $\tau_2 = 17 \mu\text{s}$ . This characteristic time  $\tau_3$  is typical for both LC cell types used in our experiments. The relaxation time  $\tau_3 = \tau_\theta = 1 \text{ ms}$  is the typical time for bulk reorientation of LC. A slow relaxation with a de-

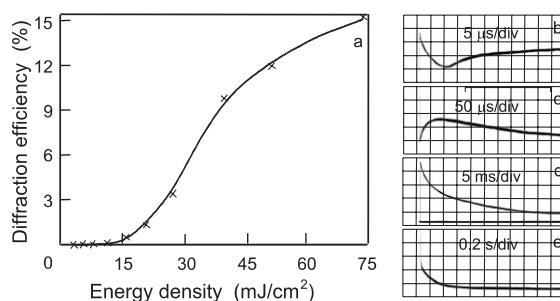


Fig. 8. (a) The dependence of the diffraction efficiency of orientational grating  $\eta$  on pump beam energy density and (b)–(e) the oscillograms of the decay of a diffraction signal from a He–Ne laser for the LC cell with azo-modified surface on different time scales. Excitation energy is  $60 \text{ mJ cm}^{-2}$ .

cay constant  $\tau_s = 1 \text{ s}$  may be caused by rearrangement of the azo-polymer surface under laser irradiation and its following recovery. Studies of the grating formation kinetics show that at high powerful excitation ( $>60 \text{ mJ cm}^{-2}$ ) within 1 s the brightness of the diffraction maxima becomes higher and a stable state sets in. This time corresponds to ultimate reorientation of the LC film. Static gratings with a spatial frequency  $120 \text{ lines mm}^{-1}$  were recorded with a single pulse at the power density of  $80 \text{ mJ cm}^{-2}$ . Their microphotograph is presented in Fig. 9. The gratings relaxed in the dark over a time period of couple of months.



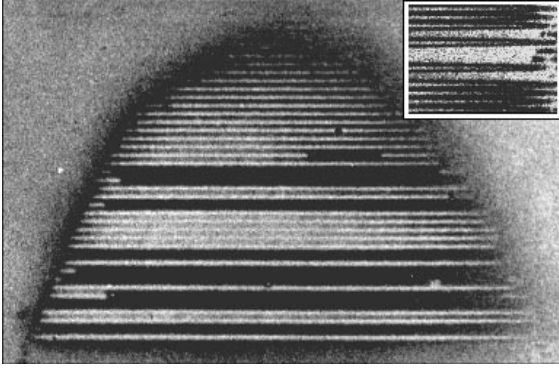


Fig. 9. The photomicrographs of the gratings with the spatial frequency 120 lines  $\text{mm}^{-1}$ .

### 3. Theoretical estimations

In both kinds of the samples one of surfaces plays important role in the molecular reorientation of LC. The output surface with PVA coating is not changed after irradiation. But along an input surface, we believe, the easy-orientation axis is induced. In the cells **II** there is initial axis of easy orientation. After illumination its position is changed. It is due to the photoisomerization of azo-dye joined to copolymer film. In the cells **I** the photoisomerization of azo-dye in the bulk of LC and surface reorganization of PVA film on input substrate take place. In this case the easy-orientation axis arises after powerful irradiation ( $80 \text{ mJ cm}^{-2}$ ).

Knowing the angle of director rotation on the input substrate, we can estimate the anchoring energy and its changes during the course of irradiation. Consider an LC cell with a thickness  $L$  where the output substrate is rubbed and the director has infinitely strong anchoring on it, while the input substrate has a finite director anchoring and the easy-orientation axis direction forms an angle  $\phi_0$  with the rubbing on the output substrate. In view of the symmetry of the problem, the director field can be described with the angle  $\phi(z)$

$$\mathbf{n}(z) = (\cos \phi(z), \sin \phi(z), 0)$$

where the  $z$ -axis is perpendicular to the cell substrates. The free energy functional takes the form

$$F = \frac{1}{2} \int_0^L K_{22}(\phi')^2 dz - \frac{1}{2} W_p \cos^2(\phi(L) - \phi_0)$$

For  $z = 0$ , the easy-orientation direction is assumed to be along Ox.  $W_p$  is the anchoring energy on the substrate for  $z = L$ , and  $K_{22}$  is the elastic constant. From the condition of minimality of the free energy functional, we obtain the Euler–Lagrange equation and the relevant boundary condition

$$\phi'' = 0$$

$$K_{22}\phi' + W_p \cos(\phi(L) - \phi_0) \sin(\phi(L) - \phi_0) = 0$$

In view of the infinitely strong anchoring on the rubbed substrate we have another boundary condition  $\phi(0) = 0$ . A solution to the Euler–Lagrange equation satisfying this condition takes the form

$$\phi(z) = a \frac{z}{L}$$

Here, the unknown constant  $a = \phi(L)$  is found from the first boundary condition

$$-\frac{2a}{\sin 2(a - \phi_0)} = \xi_p$$

where  $\xi_p = W_p L / K_{22}$ . In the general case, the constant  $a$  can only be found numerically. For the special case where  $\phi_0 = \pi/2$  (easy-orientation axis is orthogonal to the direction of light polarization) we have

$$\frac{2a}{\sin 2a} = \xi_2$$

In this case, a nontrivial solution exists only for  $\xi_2 > 1$ , which means that for  $\xi_2 \leq 1$  and infinitely strong anchoring of the director on the second substrate ( $z = 0$ ), the director distribution in the cell will be uniform  $\phi(z) \equiv 0$ . For  $\xi_2 \gg 1$ , it is easy to find a solution as an expansion in terms of  $1/\xi_2$

$$\phi(z) = \begin{cases} 0, & \xi_2 \leq 1 \\ \frac{\pi}{2} \left(1 - \frac{1}{\xi_2}\right) \frac{z}{L}, & \xi_2 \gg 1 \end{cases}$$

Then, we obtain an expression suitable for estimation of the anchoring energy and its variation in the course of irradiation:

$$W_p = \frac{K_{22}}{L} \frac{2\phi(L)}{\sin 2\phi(L)} \quad (1)$$

In the cell **I** in initial state both surfaces have strong anchoring and we can assume, that both easy axes are in the same direction  $\phi(0) = \phi(L) = 0$ . After illumination at one of the surfaces a new direction of the easy axis is induced. As a result, the director rotates towards a new easy axis and now  $\phi(L) \neq 0$ . If this new direction is perpendicular to the initial one (it is orthogonal to the light polarization), then we can estimate the anchoring energy corresponding to the new axis by the same formula (1).

(a) In the case of the azo-dye-doped LC layer (cell **I**) oriented with rubbed PVA films, we observe the emergence of an easy-orientation axis on the input substrate after illumination. The twist angle of the director rotation is equal to  $12^\circ$ . Under intensive laser excitation, the polymeric film softens and loses its initial orienting properties, resulting in an abrupt change in the anchoring energy, from an infinitely high value ( $\xi_p \gg 1$ ) to  $W$  such that  $\xi_p \geq 1$ . For value of  $K_{22} = 4 \times 10^{-11}$  N, a layer thickness of  $L = 50 \mu\text{m}$  and an angle  $\phi = 12^\circ$ , the value of the anchoring energy density is  $W \approx 10^{-8} \text{ mJ cm}^{-2}$ . The latter is characteristic of the induction of an easy-orientation axis and agrees well with other experiments [34].

(b) In the case of LC cells with an azo-polymer film (cell **II**), an easy-orientation axis is created along the polymer extension direction, which is perpendicular to the rubbing direction of the PVA layer. As a result, we have a primary twist structure with a certain angle  $\phi'$ . Fig. 6 (curve 2) illustrates the dependence of the anchoring energy density on the pumping energy and its variation in time following excitation. The anchoring energy density corresponding to the initial twist angle  $\phi' = 18^\circ$  is equal to  $W_0 = 1.1 \times 10^{-7} \text{ mJ cm}^{-2}$ . Under illumination, azo-fragments align predominantly at right angles to the light polarization. Such alignment either augments (light polarization is along the rubbing direction) or reduces the anchoring energy (polarization is normal to rubbing). Accordingly, the parameter  $a$ , together with  $\phi(L) = a$ , either increases or decreases or even becomes equal to zero, i.e. there occurs an increase (or decrease) of the director twisting or twisting disappears altogether. Thus, it is seen in Fig. 6a that in case of single-pulse excitation at an energy

density of  $80 \text{ mJ cm}^{-2}$ , when the polarization direction coincides with the rubbing direction  $\mathbf{n}$ , the director turns by  $23^\circ$  in addition to the initial angle of  $18^\circ$ . The anchoring energy rises 1.5-fold starting from a threshold pumping value equal to  $30 \text{ mJ cm}^{-2}$ . Excitation with a train of pulses at 1 Hz frequency results in the formation of a static recording (Fig. 7a and b) for which the anchoring energy is  $2.4 \times 10^{-7} \text{ mJ cm}^{-2}$ .

When illumination is sufficiently intensive, light exerts a heating effect on the orienting agent and near-surface region of the LC, in addition to the orienting action on the azo-fragments. This in turn, brings about a decrease in the anchoring energy due to lowering of the order parameter of both the azo-fragments and polymeric chains, and the LC near the surface. As a consequence, for a Gaussian beam in the domain of large light intensities, orientational ordering of azo-fragments is sufficiently high and the condition  $\xi_p \geq 1$  is satisfied; accordingly, there is a larger degree of director rotation, whereas on the beam periphery  $\xi_p < 1$  due to lower heating and there is no twisting at all. This is easily observable in static recording with the pulse train (Fig. 7c).

On the other hand, in the case of prolonged illumination, heating results in a softening of the polymer. Therefore, orientational ordering of azo-fragments entails reorientation of the basic chain of the polymer. Since at room temperature, mobility of the basic polymer chain is sufficiently small, we obtain a new stationary value of the anchoring energy and, hence, static recording. Characteristic times of reorientation of the basic chain must be fairly large and therefore, enhancement of recording after the SH pulse is possible. This explains the lagging of the recording observed in studying grating nonlinearity, which manifests itself as increased brightness of diffraction maxima in the first second after illumination.

#### 4. Discussion

In the case of intensive excitation with nanosecond laser pulses, *trans*-isomers go to an excited state from which the formation of a *cis*-isomer is highly probable. For azo-compounds, the group to

which the dyes in question belong, the lifetime of the *cis*-form is comparatively long (up to some hours for liquid-crystalline azobenzenes [32] and several minutes for azobenzene dyes in polymeric matrices [33]). The laser wavelength ( $\lambda = 533$  nm) falls within the long wavelength region of the absorption spectra of both isomers (the absorption band of *trans*-molecules is much steeper than that of *cis*-molecules [15]). This means that *cis*-isomers may go to an excited state from which they can transfer to the ground state via nonradiative conversion and transform into the *trans*-isomer upon heating or by irradiation with a longer wavelength (for example by He–Ne laser irradiation). It is possible to achieve an accumulation of *cis*-isomers in the excited state because of the lifetime of this state is determined by the metastable level ( $10^{-6}$  s). In the reorientation process, the shape change of the molecules, from the rod-like *trans*-isomer to the bent *cis*-isomer and the subsequent excitation of the *cis*-molecules are of importance. The bent *cis*-form has less polarizability and less anisotropy than the *trans*-form and as a result the attractive strengths between the *cis* and LC molecules are effectively lower than between the *trans* and LC ones. After illumination with a nanosecond pulse we can expect a change of the LC environment torque. Janossy et al. demonstrated that the magnitude and the sign of induced torque of the LC environment can depend on the relation of the molecular field strengths of the excited-state and ground-state molecules of azo-dye as well as on rotation diffusion constants in these states [10].

The dynamic grating method reveals the independence of the diffraction efficiency on the intensity of the irradiation that may be caused by the *trans*–*cis* transition saturation and by the participation of all the *cis*-molecules in the photoorientational response. This phenomenon was observed in other our experiments [35] on the absorption saturation of the LC cell doped with DMANAB. In this condition, we observe “orthogonal” reorientation to the light polarization direction after irradiation in both types of the LC samples and the director rotation in azimuthal plane. The surface changes play an unavoidable role in the reorientation in the cells with azo-dye-doped LC layer. As a consequence of laser heating of ab-

sorbing LC layer with high dye concentration, the PVA film softens and loses its orienting properties. However, orientation of the LC layer near the film surface retains its directivity. The mechanism that may be occurring here is light-induced anisotropic adsorption of the dye. This phenomenon has been discovered and studied in Ref. [12]. Upon heating, *cis*-isomers are actively transformed to *trans*-isomers whose molecules are adsorbed on the film and their long axes orient themselves in such a manner that the director near the surface deviates from the light polarization. We observe an easy-orientation axis along the transformed PVA film.

Previously, we studied thermal and orientational effects in LCs doped with bleachable [36], absorbing and ionic dyes [29,31], induced by nanosecond pulses in pump–probe–beam experiments. In LCs activated with such dyes, the amplitude of the thermal component on decay traces is several times higher than that of the orientational component [36]. It should be noted that for these dye-doped LC compositions, the absorption energy density  $\alpha P$  at which the grating efficiency was measured was equal to  $25\text{--}30\text{ J cm}^{-3}$ , which is even higher than the value  $\alpha P = 20\text{ J cm}^{-3}$  used in our experiment. On the base of these data we assume that the substantial part of the monopulse energy goes to the *trans*–*cis* conformation of the molecules, but not to the heating.

Reorientation associated with mass transfer in the bulk, investigated by dynamic holography method, has an evolution time in the millisecond range as in the case of, for example, electrohydrodynamic instabilities in LCs doped with polymethyne dyes [29]. If the optical field alone caused changes in the director orientation, then the orientational component would decay after the termination of the monopulse. In azo-dye-doped LCs, the opposite effect is observed, i.e. the amplitude of the orientational component grows after the thermal decay during  $15\text{ }\mu\text{s}$ . This growing is most pronounced for the radiation intensities, which resulted in the recording of the static spot on PVA film described above. This time approximately coincides with the orientational response in the LC cell with azo-modified surface. We can see a similar behavior in the reorientation dynamics after illumination by a nanosecond pulse in both

types of samples, namely the inertia of the optical response of LC molecules during 15–17  $\mu\text{s}$ .

## 5. Conclusion

The photoorientational response of LC molecules has been studied using the dynamic holography method and the polarimetric technique in pump–probe–beam experiments. It was demonstrated that in the cells with azo-dye-doped LC layer, as well as in the LC cells with an azo-modified surface, the photoisomerization of the dye molecules and surface rearrangement control the director reorientation. The following reorientation regularities were found:

(1) The reorientation in the azo-dye-doped LC layer as well as the reorientation in the bulk of LC caused by the azo-modified surface are both characterized by an azimuthal rotation of the LC molecules. As shown by the dynamic grating method the effect develops during 15–17  $\mu\text{s}$ .

(2) In the cells **I** with an orienting PVA coating both photoreorganization of PVA film and the photoisomerization of the dye in the bulk initiate the induction of the easy-orientation axis on the surface of the input substrate.

(3) Upon laser irradiation, the azo-modified surface with the initial easy-orientation axis can cause up-twisting or untwisting of the layer director depending on the direction of the polarization vector and the radiation intensity.

(4) The anchoring energy for two types of samples was estimated. One of them (the cells **I**) had infinitely strong anchoring on substrates. After irradiation at one of the substrate the easy-orientation axis was induced. In the other sample (the cells **II**) there were finite director anchoring and the easy-orientation axis along azo-polymer film before illumination. After exposure the easy axis changed its direction. The expression suitable for evaluation of the anchoring energy and its variation in the course of irradiation was obtained. The typical value of the anchoring energy density in the first kind of the samples is  $10^{-8} \text{ mJ cm}^{-2}$ , for the second kind of the samples this value is chan-

ged during increasing of pump intensity from  $10^{-7}$  to  $2.4 \times 10^{-7} \text{ mJ cm}^{-2}$ .

(5) The static gratings can be recorded by the laser irradiation field at an energy density of  $80 \text{ mJ cm}^{-2}$  in the LC cell with an azo-polymeric coating, their spatial frequency was not less than  $100 \text{ lines mm}^{-1}$ .

## Acknowledgements

The authors are grateful to Dr. V.A. Grozhik and Dr. N.A. Usova for helpful discussions. Financial support from the international fund INTAS-BELARUS (grant N 97-0635) is gratefully acknowledged.

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